# Measurement report: The influence of traffic and new particle formation on the size distribution of 1-800 nm particles in Helsinki: a street canyon and an urban background station comparison

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Abstract. Most of the anthropogenic air pollution sources are located in urban environments. The contribution of these 14 15 sources to the population of atmospheric particles in the urban environment is poorly known. In this study, we investigated 16 the aerosol particle number concentrations in a diameter range from 1 to 800 nm at a street canyon site and at a background 17 station within 1 km from each other in Helsinki, Finland. We use these number size distribution data together with 18 complementary trace gas data and develop a method to estimate the relative contributions of traffic and atmospheric new 19 particle formation (NPF) to the concentrations of sub-3 nm particles. During the daytime, the particle concentrations were 20 higher at the street canyon site than at the background station in all analyzed modes: sub-3 nm particles, nucleation mode 21 (3-25 nm), Aitken mode (25-100 nm), and accumulation mode (100-800 nm). The population of sub-3 nm and nucleation 22 mode particles was linked to local sources such as traffic, while the accumulation mode particles were more related to 23 non-local sources. Aitken mode particles were dominated by local sources at the street canyon site while at the background 24 station they were mainly influenced by non-local sources. The results of this study support earlier research showing direct 25 emissions of the sub-3 nm particles from traffic. However, by using our new method, we show that during NPF events, 26 traffic contribution to the total sub-3 nm particle concentration can be small and during daytime (6:00-20:00) in spring it 27 does not dominate the sub-3 nm particle population at either of the researched sites. In the future, the contribution of 28 traffic to particle number concentrations in different urban environments can be estimated with a similar approach, but 29 determining the relationships between the gas and particle concentrations from observations needs to be conducted with longer data sets from different urban environments. 30

## 31 1. Introduction

Aerosol particles are both directly emitted to the atmosphere (primary particles) and formed from gaseous precursors (secondary particles) (Kulmala and Kerminen, 2008). Secondary particles can form by new particle formation (NPF) via atmospheric photochemical reactions or nucleate in plumes from local sources (Kerminen et al., 2018; Mylläri et al., 2016). Additionally, particles may form while hot vehicle exhaust is cooled and diluted, which is called delayed primary particulate matter formation (Rönkkö and Timonen, 2019). The urban environment contains a mixture of secondary particles, and primary particles emitted from a variety of industrial processes, traffic, power generation, and natural sources (Seinfeld and Pandis, 2016). Aerosol particles influence the visibility (Hyslop, 2009), the hydrological cycle 39 (Rosenfeld et al., 2008), and radiation balance (Andreae, 2009; Ramanathan and Feng, 2009). Furthermore, particles can 40 harm human health, impacting respiratory and cardiovascular systems (André, 2014). Models show that outdoor air 41 pollution causes approximately 400 000 premature deaths in Europe annually (Geels et al., 2015; Im et al., 2018), from 42 which around 2000 occur in Finland (Im et al., 2019). However, nanoparticles have different health impacts than larger 43 particles. Urban air pollution contains magnetite nanoparticles, which accumulate in the brain and may cause 44 neurodegenerative diseases (Maher et al., 2016). Nanoparticles with diameters below 3 nm may have significant, so far 45 poorly understood, health effects due to their nose-to-brain transport via the olfactory pathway (Tian et al., 2019). Hence,

- 46 a better understanding of the concentrations, sources and health impacts of the nanoparticles will improve the estimates
- 47 of adverse health effects of urban pollution sources.

48 In recent years, instrument development has enabled the detection of aerosol particles with diameters between 1 and 3 nm 49 (Vanhanen et al., 2011), which we here refer to as sub-3 nm particles. This had made it possible to study the very beginning of NPF, which starts with the formation of sub-3 nm particles. Regional NPF events, where the growth of the 50 51 particles to larger sizes can be followed, are favored in specific meteorological conditions, for example, high solar 52 radiation and low relative humidity, as well as an abundance of low-volatile gaseous precursors (Hussein et al., 2008; 53 Kerminen et al., 2018; Salma et al., 2011; Wonaschütz et al., 2015). One of the known gaseous precursors, which plays 54 an important role in NPF, is sulfuric acid (SA). SA is an oxidation product of sulfur dioxide (SO<sub>2</sub>), which is primarily 55 emitted from anthropogenic processes related to fuel combustion, for example from traffic. Previous studies have shown 56 that in addition to indirect emission of SA, resulting from the oxidation of traffic-emitted SO<sub>2</sub> (Olin et al., 2020), SA is 57 also emitted directly from traffic (Arnold et al., 2012; Rönkkö et al., 2013). In many locations, SA concentration is one 58 of the critical factors determining whether an NPF event occurs (Kuang et al., 2008; Ripamonti et al., 2013; Wang et al.,

**59** 2011).

60 In addition to NPF, traffic is a significant source of sub-3 nm particles (Hietikko et al., 2018; Rönkkö et al., 2017). The 61 sub-3 nm particles are directly emitted from vehicle exhaust (Rönkkö et al., 2017; Sgro et al., 2012) and brake wear 62 (Nosko et al., 2017) or formed in the exhaust plume from the nucleating gaseous components (Rönkkö and Timonen, 63 2019). The concentrations from the road emissions decrease fast while moving away from a road due to dispersion (Pirjola 64 et al., 2006). Especially, the concentration of the sub-3 nm particles is additionally reduced by condensation and 65 coagulation (Kangasniemi et al., 2019). Rönkkö et al. (2017) showed that the sub-3 nm particles represent 20-54% of the 66 particle population in a 'semiurban' roadside environment in Helsinki. Kontkanen et al. (2017) analyzed the sub-3 nm 67 particle concentrations in different environments and concluded that the sub-3 nm particle concentrations are higher in 68 locations influenced by anthropogenic emissions. Hietikko et al. (2018) observed elevated concentrations of sub-3 nm 69 particles at the street canyon in Helsinki during rush hours and when wind was coming from the road, and concluded that 70 sub-3 nm particles are linked to traffic activity. In addition, they found that high sub-3nm particle concentrations coincided with high concentrations of larger particles suggesting the importance of traffic emissions. Traffic emissions do not only 71 72 contain particles but also SA, volatile organic compounds, and trace gases, such as carbon dioxide (CO<sub>2</sub>) and nitrogen 73 oxides (NO<sub>x</sub>), which are commonly used as traffic markers. Generally, the impacts of traffic on urban air quality and on 74 human health is still not well quantified.

Previously, particle size distributions have been measured in different urban environments, such as London (Bousiotis et al., 2019; Harrison et al., 2019; Hofman et al., 2016), Stockholm (Mårtensson et al., 2006), Innsbruck (Deventer et al., 2018), Los Angeles (Zhu et al., 2002), Beijing (Zhou et al., 2020), Shanghai (Xiao et al., 2015), and Helsinki (Hussein et

78 al., 2006; Ripamonti et al., 2013). In the Helsinki area, the focus of the research has been either on NPF events (Hussein 79 et al., 2008, 2009) or the primary particle emissions (Hietikko et al., 2018; Ripamonti et al., 2013; Rönkkö et al., 2017). 80 These approaches leave an open question about the relative contribution of each source to the particle population. To 81 answer this question, we conducted simultaneous measurements at two close-by stations in the Helsinki area: at the street 82 canyon and at the urban background station. For the first time, particle size distributions in a diameter range from 1 to 83 800 nm as well as the concentrations of precursor gases were simultaneously measured at two nearby stations in Helsinki. 84 In this article, we present the results of these measurements and compare the particle size distributions and their variation 85 at these two stations. Specifically, we develop and apply a new method to determine the relative contributions of NPF 86 and traffic to the sub-3 nm particle population in different urban environments.

## 87 2. Methods

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## 2.1. Measurement stations

89 We performed measurements at two different stations in Helsinki, Finland, during April-June 2018. The first one is the 90 Helsinki Region Environmental Services (HSY) air quality station, which is placed in a street canyon (approximately 0.5 91 m from the edge of Mäkelänkatu street), and represents a busy street environment (with approximately 28 100 vehicles 92 per workday) (Kuuluvainen et al., 2018). The second one, the Station for Measuring Ecosystem-Atmosphere Relations 93 (SMEAR III), is located within 900 m north-east of HSY site, and it is classified as an urban background station (Fig. 1) 94 (Järvi et al., 2009). The sites are separated by buildings, a botanic garden, and a small deciduous forest. The SMEAR III 95 is located on a hill, approximately 12 m above the nearest busy road (Hämeentie street). The SMEAR III is separated 96 from Hämeentie by a 150 m band of a deciduous forest. Apart from the forest, in the SMEAR III surrounding are also 97 buildings, parking lots, and small vegetation (Järvi et al., 2009). In this article, the two measurement stations are called 98 'street canyon' and 'background', respectively.



99 Figure 1. Aerial photography (a) and 3d model (b) of stations: street canyon (red) and background (yellow). The100 photograph and the model were provided by The City of Helsinki map service (CC BY 4.0).

## 101 2.2. Measurement period and comparison of data from sites

102 We measured particle number size distribution, trace gas and SA concentrations at both stations during the period 27 April

103 2018 – 5 June 2018. An overview of instruments used during this campaign is presented in Table 1 indicating the total

104 running time at each station. The detailed working time for each instrument is shown in Table A1. Most of the analysis 105 was conducted separately for workdays and days free of work, i.e. weekends and holidays (1 May 2018 and 10 May 106 2018), which are for simplicity just referred to as 'weekends' in this article. When comparing particle concentrations from 107 two stations, we analyze times when all the instruments measuring particles were performing at each site. This resulted 108 in 120 and 101 hours of measured particle concentration during weekends and workdays, respectively, at the street canyon 109 site. At the background station, it resulted in 217 hours of observed particle concentration during weekends and 398 hours 110 during workdays. In addition, we present separately a few case studies, where the overlapping data obtained 111 simultaneously from two stations are analyzed in more detail. Oppositely to the analysis of particle concentrations, 112 sulfuric acid (SA) concentration and condensation sink (CS) were studied only for the overlapping period of SA 113 concentration measurements at two stations resulting in 167 and 329 hours measured during weekends and workdays, 114 respectively.

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## 2.3. Particle size distribution measurement

116 A wide range of particle size distribution was obtained by combining several instruments: a Particle Size Magnifier (PSM)

117 (Vanhanen et al., 2011), an Ultrafine Condensation Particle Counter (UCPC), and a Condensation Particle Counter (CPC)

118 (Kangasluoma and Attoui, 2019) as well as a Differential Mobility Particle Sizer (DMPS) (Wiedensohler et al., 2012).

119 The measured size ranges and working hours of these instruments are presented in Table 1. At the street canyon site,

120 particle size distribution was measured at 4 m height, while at the background station at 1.5 m.

121 The PSM technique contains a pre-conditioner, that activates the smallest particles and grows them up to 90 nm, and a 122 CPC (Vanhanen et al., 2011). The minimum size of activated particles depends on the diethylene glycol supersaturation 123 in the pre-conditioner (Lehtipalo et al., 2014). Altering the supersaturation condition allows varying the minimum size of 124 activated and measured particles between 1 and 3 nm. The PSM can be used to measure particle concentrations in three 125 different modes: fixed, step, and scanning. In the fixed mode, supersaturation and the minimum size of the measured 126 particles are constant. Data obtained by measuring in the fixed mode have a high temporal resolution (1 s), and therefore 127 it is mainly used in a very rapidly changing environment such as a busy street. In the step mode, supersaturation and the 128 lowest size of measured particles oscillate between three set values. This allows analyzing particle size distribution in the 129 range from 1 to 3 nm. On the other hand, data obtained from step mode measurements have a lower temporal resolution 130 (3 min). Adjusting the time of every supersaturation measurement allows minimizing the uncertainties related to the rapid 131 changes in the analyzed environment. In the scanning mode, supersaturation gradually changes between two set values. 132 The scanning mode enables choosing the size bins when inverting the raw data to a size distribution. However, the 133 temporal resolution of scanning mode is the lowest of all the modes (4 min). In the scanning mode, we assume that particle 134 concentration stays constant during each scan, thus this mode cannot be used in a rapidly changing environment. In this 135 study, PSM was operated in fixed and step modes. At both stations, PSMs working in the fixed mode measured 136 concentrations of particles with sizes larger than 1.2 nm.

137 Condensation particle counters enlarge particles by condensation of supersaturated condensable vapors. Once particles 138 reach a size sufficient for optical detection, they are counted by the optical particle counter. In this study, we use two 139 models of butanol-based CPCs, from which one measures particle concentration of particles with sizes larger than 3 nm,

140 while the other one counts particles with sizes larger than 7 nm. For simplicity, we call them UCPC and CPC, respectively.

- 141 Differential mobility particle sizer (DMPS) consists of a differential mobility analyzer (DMA) and a CPC. The DMA
- 142 classifies charged particles according to their mobility in an electric field. By incrementally stepping the voltage applied
- to the central rod of the DMA, particles of corresponding mobility can be classified by the DMA and further quantified

by the CPC. During an 8 minute cycle, DMPS monitors the size distribution of particles with a diameter between 6

- and 800 nm. The size distribution obtained from DMPS measurements was used to study the loss rate of vapors due to
- 146 condensation on existing particles, i.e. CS (Kulmala et al., 2012). DMPS data from the background station was also
- 147 utilized to identify NPF events based on the method proposed by Dal Maso et al. (2005).
- All instruments were corrected for diffusion losses in their inlets except the UCPC measuring at the background station,in which the core sampling technique (Fu et al., 2019) was used.
- Sub-3 nm particle concentration was determined by subtracting concentration measured by the UCPC from concentrations 150 151 measured by the PSM working at the fixed mode. The nucleation mode (3-25 nm) particle concentration was computed by adding concentration measured by DMPS with diameters of 7-25 nm to the difference of concentration measured by 152 153 CPC and UCPC. Particle concentrations measured by DMPS with diameters of 25-100 nm and 100-800 nm were 154 considered the Aitken and accumulation mode concentrations. The size range for the Aitken mode corresponds to the range of mean particle size in the typical soot mode of vehicle exhaust (Rönkkö and Timonen, 2019). At the street canyon 155 156 site, gaps in the UCPC data were filled with the concentration of particles larger than 3 nm obtained from the PSM 157 measuring in the step mode. At the background station, UCPC data from 29 May to 4 June were corrected by checking 158 that the ratios of concentrations measured with the PSM and UCPC as well as UCPC and CPC agree in the night-time 159 (see Suplement). All the measured size ranges correspond to the mobility diameter of particles.
- 160 Table 1. Overview of the main instruments used at the street canyon and background station during the campaign.

		Working time	Working time at
Instrument	Description	at street	background
		canyon [h]	station [h]
PSM (fixed mode)	Concentration of particles larger than 1.2 nm	246	766
PSM (step mode)	Particle size distribution in the range of 1-3 nm	833	-
UCPC	Concentration of particles larger than 3 nm	548	670
СРС	Concentration of particles larger than 7 nm	750	728
DMPS	Particle size distribution in the range of 6-800 nm	840	821
CI-APi-TOF	Concentration and chemical identification of vapor molecules and molecular clusters in size range approximately 0.1-1 nm. In this study only sulfuric acid concentration is utilized.	501	776
SO <sub>2</sub> analyzer	Concentration of SO <sub>2</sub> on ppb level	452	937
CO <sub>2</sub> analyzer	Concentration of CO <sub>2</sub> on ppm level	771	248
NO/NO <sub>x</sub> analyzer	Concentration of NO/NO <sub>x</sub> on ppm level	937	937

#### 2.3.1. Uncertainties of sub-3 nm particles measurement

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Measuring the concentration of particles smaller than 3 nm contains noteworthy uncertainties mainly due to the effect ofchemical composition and charging state of particles on the cutoff size of PSM.

Particle detection efficiency in butanol counters (Wlasits et al., 2020) and the PSM techniques depend strongly on the chemical composition of measured clusters. Experiments show that the difference between the cutoff diameter in PSM for particles with different chemical composition can reach up to approximately 1 nm (Jiang et al., 2011; Kangasluoma et al., 2014, 2016). This causes uncertainty of  $\pm$  0.5 nm for particles with unknown chemical composition. PSM calibrated with particles with the same chemical composition as measured one would have a negligible offset (Kangasluoma et al., 2015). In the urban environment, the chemical composition of particles is complex and evolving with time, thus this uncertainty cannot be minimized in this research.

172 Uncertainty due to the charging state of particles is mainly affected by the discrepancy between the charging state of 173 measured particles and particles used for the calibration. PSMs were calibrated with negatively charged tungsten oxide 174 clusters by the method presented in Kangasluoma et al. (2015). However, the majority of particles measured in the urban 175 environment are likely electrically neutral (Yao et al., 2018). Since neutral particles are activated at a higher 176 supersaturation than charged particles, we probably underestimate the size of measured particles (Kangasluoma et al., 177 2016, 2017; Winkler et al., 2008). Experiments indicate a 0.1-0.5 nm increase in the activated diameter of neutral particles 178 in PSM in comparison to the charged ones (Kangasluoma et al., 2016, 2017). When the effect of charge on the measured 179 particle population is unknown, increasing the cutoff diameter in PSM by 0.3 nm will reduce the uncertainty of the state 180 of charge to  $\pm 0.2$  nm (Kangasluoma and Kontkanen, 2017).

Additionally, meteorological conditions such as humidity can affect the cutoff size of PSM and CPC (Kangasluoma et al., 2013; Tauber et al., 2019).

Lastly, the non-ideal efficiency curve, used for determining the cutoff diameter, makes it possible to sample particles
smaller than the cutoff size. When the relative contribution of sub-3 nm particles to the total particle population is high,
the uncertainties of cutoff diameter or the shape of the efficiency curve can affect the total concentration measured by
PSM and CPC (Kangasluoma and Kontkanen, 2017).

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# 2.4. Sulfuric acid measurement

Sulfuric acid (SA) concentration was monitored with a high-resolution chemical ionization atmospheric pressure interface 188 189 time-of-flight mass spectrometer (CI-APi-TOF) with nitrate ( $NO_3^{-}$ ) as a reagent ion. CI-APi-TOF technique contains a 190 chemical ionization source (CI) and an atmospheric pressure interface (APi) coupled with a time-of-flight mass 191 spectrometer (TOF). Chemical ionization is a soft ionization technique in which the reagent ion reacts with analyzed 192 compounds and charge them. NO<sub>3</sub> is a reagent ion used for the detection of gaseous SA in ambient air (Eisele and Tanner, 193 1993; Jokinen et al., 2012; Mauldin et al., 1999).  $NO_3^-$  or its cluster with nitric acid (HNO<sub>3</sub>NO<sub>3</sub><sup>-</sup>) reacts via proton transfer 194 reaction with sulfuric acid creating a cluster detectable by the APi-TOF technique (Jokinen et al., 2012). A detailed 195 description of nitrate-based CI method used as a pre-treatment for APi-TOF technique is presented by Jokinen et al. 196 (2012). The atmospheric pressure interface guides ionized compounds through three stages of lowering sample pressure

to the time-of-flight region. A TOF mass spectrometer separates and detects analyzed compounds by their mass-to-charge
 ratios. A detailed description of the APi-TOF technique is described by Junninen et al. (2010).

199 Due to the uncertainty of the rate of the reaction between gaseous sulfuric acid and the nitrate ion, the CI-APi-TOF needs 200 to be calibrated by taking the wall losses of SA inside the instrument and the flow conditions of the ion source into

201 consideration (Kürten et al., 2012; Viggiano et al., 1997). Calibration of CI-APi-TOF was done before the campaign,

based on the method proposed by Kürten et al. (2012). The SA concentration was calculated from Eq (1) (Jokinen et al.,
2012).

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$$[SA] = C \cdot \frac{CR_{97} + CR_{160}}{CR_{62} + CR_{125} + CR_{188}}$$
(1)

where [SA] is SA concentration, C is the calibration coefficient and  $CR_M$  is a count rate of an ion with a mass M in amu.

207 The SA zero level concentration, determined by measuring filtered air, was subtracted from the measured concentrations.

208 Uncertainties of the averaged absolute concentration measured by CI-APi-TOF are in the order of 50%, while the

uncertainties of relative changes in the concentration are smaller than 10% (Ehn et al., 2014), thus comparing SA

- 210 concentration values between stations is not as accurate as analyzing time series of SA and other variables.
- 211 2.5. Other instrumentation

Nitric oxide (NO),  $CO_2$ ,  $SO_2$ , and  $NO_x$  were additionally measured during this campaign (Table 1). To complement these measurements, we used continuous measurements performed at both stations. These include meteorological parameters, ozone ( $O_3$ ) concentration, ion size distribution, and black carbon (BC) concentration. All the instruments used are listed in Table A2.

## 216

#### 2.6. Estimation of the relative contribution of NPF and traffic to sub-3 nm particles

217 To estimate the influence of traffic and NPF on the sub-3 nm particle population, we analyzed the correlation between 218 sub-3 nm particles and  $NO_x$  concentrations as well as between sub-3 nm particles and SA concentrations.  $NO_x$ 219 concentration was used as a traffic marker (Olin et al., 2020) while SA concentration was used as an NPF marker (Sipila 220 et al., 2010). We separately investigated the relation between SA and NO<sub>x</sub> concentrations in the street canyon, in order to 221 justify the use of SA as a tracer for NPF even though emissions of SA from traffic have previously been reported (Arnold 222 et al., 2012; Olin et al., 2020). Bivariate fittings (Cantrell, 2008; Williamson, 1968; York, 1966) were conducted on the 223 common logarithms of sub-3 nm particles and SA, when NOx concentration was low, to estimate sub-3 nm particles 224 concentration originating from NPF. Correlation between common logarithms of sub-3 nm particles and NO<sub>x</sub>, when SA 225 concentration was low, was used to estimate sub-3 nm particle concentration originating from traffic. Equations used for 226 calculating sub-3 nm particles emitted by traffic and NPF as well as their relative contributions to the particle population 227 are presented in the Appendix (Eq. A1-A6).

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#### 231 **3.** Results and Discussion

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#### 3.1. NPF event classification

233 The results of the NPF event classification at the background station for the studied period is shown in Table 2. The

- examples of an event, non-event, and undefined class are shown in Fig. S2. The overall frequency of NPF event days was
- 235 12.5%; 21% of weekends and 8% of workdays were classified as events. Due to nucleation mode particles originating
- from local sources, the majority of days were classified as undefined.

Table 2. NPF event classification at the background station for the period 27 April 2018 – 5 June 2018. Results are
 presented separately for a full campaign, weekends, and workdays.

Class	Date	Freq <sub>campaign</sub>	Freqweekends	Freqworkdays
Event	5.05, 7.05, 10.05, 13.05, 28.05	12.5%	21%	8%
Non-event	29.04, 1.05, 6.05, 11.05-12.05, 15.05, 21.05, 26.05, 3.06	22.5%	43%	11%
Undefined	27.04-28.04, 30.04, 2.05-4.05, 8.05-9.05, 14.05, 16.05-	65%	36%	81%
Ondernied	20.05, 22.05-25.05, 27.05, 29.05-2.06, 4.06-5.06	0570	5070	0170

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## 3.2. Particle size distributions

240 Figure 2 presents the median particle size distributions at both stations during workdays and weekends at different times of the day. The shape of the size distributions for Aitken (25-100 nm) and accumulation mode (100-800 nm) particles is 241 242 quite similar at the two sites in most of the cases, but the concentrations are higher at the street canyon, as discussed later in this section. What stands out is almost constant Aitken mode measured during daytime on workdays at the street canyon 243 244 site. At the street canyon site, the concentration of particles in the nucleation mode (3-25 nm) has a decreasing trend with 245 an increase of particle size, except for the nighttime on workdays. At the background station, during the night and 246 afternoon, the concentration of particles in nucleation mode increases with increasing particle diameter. During noon the 247 nucleation mode has a peak above 10 nm, likely linked to NPF events. A sudden change in concentrations of particles 248 with a diameter below and above 7 nm at the background station can be associated with the uncertainty of the different 249 instruments used for measuring particles smaller than 10 nm (Kangasluoma et al., 2020). The shape of the particle size 250 distribution at the background station is somewhat different from the average size distribution measured at the same 251 location in the years 1997-2003 (Hussein et al., 2004). Hussein et al (2004) found that during spring the size distribution 252 of 8 and 400 nm particles reaches the maximum concentration in the nucleation mode, while in our study concentration 253 of particles within the same size range has a maximum in the Aitken mode. This difference could be explained by a higher 254 contribution of NPF to the average size distribution determined by Hussein et al (2004). At the street canyon site, the 255 shape of the size distribution of larger than 5 nm particles observed in our study is quite similar to the one measured at 256 the same location in May 2017 (Hietikko et al., 2018). In 2017, the particle concentration was observed to reach a 257 maximum for particles around 5 nm (Hietikko et al., 2018), while in our case the highest concentration during daytime is 258 reached for particles smaller than 3 nm.

Focusing on the smallest particles (Fig. 3), we observe that at the street canyon the median concentration of sub-3 nm particles is up to 2.4\*10<sup>4</sup> cm<sup>-3</sup> higher than at the background station (Fig. 3c). The concentration of sub-3 nm particles is higher at the street canyon site regardless the particle loss due to coagulation scavenging being twice as high as at the 262 background station (discussed later in this section). At the street canyon, two traffic-related peaks are observed during the 263 morning (6:00-8:00) and afternoon hours (15:00-17:00) on workdays. These peaks correspond to the increase of  $NO_x$ 264 concentration at the street canyon site during workdays (Fig. S4a). During weekends, there is no morning peak and the 265 afternoon peak occurs earlier (14:00-17:00). The level and the diurnal variations of sub-3 nm particles at the street canyon 266 is similar to observations at the same site in May 2017 by Hietikko et al. (2018). They found that sub-3 nm particles 267 followed the pattern observed in numbers of vehicles at Mäkelänkatu street. However, in 2017 the morning peak in 268 sub-3 nm particles was shorter and the afternoon peak started one hour earlier. At the background station, the diurnal 269 variation of sub-3 nm particle concentration has a maximum around noon both during weekends and workdays. 270 Nevertheless, a sharp increase of sub-3 nm particles concentration is observed in the morning (6:00) during workdays. 271 The morning raise of sub-3 nm particle concentration at the background station during workdays corresponds to a peak 272 of NO<sub>x</sub> concentration (Fig. S4b), which suggests the contribution of traffic emissions. The absence of clearly visible 273 traffic-related peaks at the background station can be caused by the 150 m distance of the site uphill from the nearest road 274 as well as the separation of the road and the station by the forest. The midday maximum of sub-3 nm particles 275 concentration is likely related to NPF. However, Kontkanen et al. (2017) showed that at the background station the starting 276 time of a sub-3 nm particle concentration increase varies hardly throughout the year, meaning that the increase in sub-3 nm 277 particles concentration is independent of the sunrise, respectively solar radiation. This suggests that traffic at least partially 278 influences the observed midday peak in sub-3nm particle concentration at the background station.

The difference between the stations (Fig. 3c) shows that median sub-3 nm particle concentrations during the rush hours in the street canyon site are clearly higher than at the background station throughout, roughly by a factor of 5. However, the concentrations are slightly higher also during nighttime, which shows the influence of the continuous traffic emissions at the street canyon site. One should keep in mind, though, that data presented in Fig. 3 can be affected by the differences in measurement period between the two sites, especially if the fraction of data collected during NPF event is different.



Figure 2. Median particle size distribution (a,c) at the street canyon and (b,d) at the background station. The colors indicate
different periods of the day: night (1:00-4:00 LT, black), morning (6:00-9:00 LT, blue), noon (10:00-13:00 LT, green),
and afternoon (15:00-18:00, red). The top row presents size distribution measured during weekends (a,b) and the bottom
one during workdays (c,d). Median size distribution was determined by DMPS (particles with sizes between 6-800 nm)

marked with solid lines in the figure, UCPC and CPC (3-7 nm), and PSM and UCPC (1-3 nm) marked with dots. This
figure with the linear y-axis can be found in Supplementary material (Fig. S3).



Figure 3. The diurnal variation of sub-3 nm particle concentration during weekends (red) and workdays (blue) (a) at the street canyon and (b) at the background station, and (c) the difference between median sub-3 nm particles concentration at the street canyon (a) and at the background station (b). The median diurnal variation is shown as a solid line with markers; the 25<sup>th</sup> and 75<sup>th</sup> percentile ranges are presented as shaded areas.

294 The diurnal variation of nucleation mode particle concentration is similar to that of sub-3 nm particles at both stations 295 (Fig. 4). During workdays, we can see traffic-related peaks, which are less pronounced on weekends. The concentrations of nucleation mode particles in the street canyon are  $10^3$ - $3.9 \times 10^4$  cm<sup>-3</sup> higher than at the background station during the 296 daytime. Concentrations of Aitken mode particles at the street canyon site are up to  $5 \times 10^3$  cm<sup>-3</sup> higher than at the 297 298 background station on workdays. During nighttime and weekends, concentrations of Aitken mode particles are similar at 299 both stations, which suggests a similar origin of these particles. The diurnal variation of Aitken mode particle 300 concentration at the background station is similar during workdays and weekends, however, during daytime 301 concentrations are higher on workdays. At street canyon during workdays, we can observe traffic-related peaks in Aitken mode particles, which are absent during weekends. Accumulation mode particle concentrations during workdays and 302 303 weekends are comparable at each of the stations (Fig. S5). During daytime accumulation mode particles reached higher concentrations at the street canyon than at the background station, which causes a difference of roughly a factor of two 304 305 between condensation and coagulation sinks at the sites (Fig. 5). Accumulation mode particle concentration is almost 306 constant during the whole day.

Overall, the influence of traffic on the particle population at the street canyon is clearly visible for sub-3 nm, nucleation mode, and Aitken mode particles, while the accumulation mode is only slightly influenced by traffic. The particle concentrations at the background station are also influenced by traffic, but not as strongly as at the street canyon station. At the background station, the influence of traffic can be observed only for sub-3 nm and nucleation mode particles. These results suggest that sub-3 nm and nucleation mode particle concentrations in the urban environment are mainly influenced by local sources, while the accumulation mode particle concentrations are mostly dominated by transport from non-local sources. Whether the Aitken mode is primarily dominated by local or non-local sources depends on the analyzed location.



Figure 4. Diurnal variations of nucleation (3-25 nm), Aitken (25-100 nm), and accumulation (100-800 nm) modes particle concentration during weekends (red) and workdays (blue) measured at the street canyon (top) and background station (middle) as well as the difference between the street canyon site and the background station concentrations (bottom). The median diurnal variations are shown as solid lines with markers; the 25th and 75th percentile ranges are presented as shaded areas. This figure with the linear y-axes can be found in Supplementary material (Fig. S5).



Figure 5. The diurnal variation of CS during weekends (red) and workdays (blue) (a) at the street canyon and (b) at the background station. The median diurnal variation is shown as a solid line with markers; the 25<sup>th</sup> and 75<sup>th</sup> percentile range are presented as a shaded area.

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#### 3.3. Sulfuric acid

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326 SA concentration had a clear daytime maximum at both sites (Fig. 6). The only difference in SA concentration between 327 workdays and weekends at each site was observed during midday (13:00-15:00) when SA concentration reached higher 328 values during weekends than weekdays. During weekends, the median SA concentration at the background station had a maximum of 1.1\*10<sup>7</sup> cm<sup>-3</sup> while during workdays, it reached only 4.6\*10<sup>6</sup> cm<sup>-3</sup>. A similar pattern is observed at the street 329 canyon station with the maximum concentrations of 6.9\*10<sup>6</sup> cm<sup>-3</sup> and 3.6\*10<sup>6</sup> cm<sup>-3</sup> during weekends and weekdays, 330 331 respectively. This difference is likely linked to a bigger fraction of NPF events days during analyzed weekends than 332 workdays (Table 2). Daytime median SA concentrations are slightly higher at the background station than at the street 333 canyon (Fig. 6, Fig. S6), which is probably caused by higher CS at the street canyon site (Fig. 5). Nighttime median SA 334 concentrations are as high at the street canyon site as at the background station. SA concentrations at the street canyon 335 site are slightly lower than the concentrations measured one year earlier by Olin et al. (2020).



Figure 6. The diurnal variation of sulfuric acid (SA) concentration (a) at the street canyon and (b) at the background
station. The median diurnal variation is shown as a solid line with markers; the 25th and 75th percentiles are presented
as a shaded area.

## **340 3.4.** Case studies

To understand the behavior of sub-3 nm particles on a shorter time scale, we analyzed two periods, when the particle 341 342 concentration data are available from both sites: Saturday 5 May 2018-Sunday 6 May 2018 and Tuesday 8 May 2018 343 09:00-Wednesday 9 May 2018 15:00. The first investigated case is a weekend starting with an NPF event (Fig. 7a,b). The 344 second case contains typical workdays (Fig. 7c,d), which are classified as undefined days in the NPF event classification. 345 Supporting information about atmospheric conditions, trace gas concentrations, black carbon (BC) concentration, and CS 346 during the analyzed cases are presented in Fig. S7-S9. In both studied cases, sub-3 nm particles and SA concentrations 347 follow each other closely at the background station (Fig. 8). Oppositely, at the street canyon site, there are many 348 traffic-related sub-3 nm particles peaks, which often do not have their counterparts in SA time-series. The correlation 349 between sub-3 nm particles and SA is much weaker at the street canyon site than at the background station for both case 350 studies (Fig. S10). This suggests that the majority of SA is not originating from direct emissions from traffic. Our analysis 351 also supports studies showing that sub-3 nm particles are not only formed by clustering of atmospheric vapors, but they 352 are also directly emitted from traffic (Hietikko et al., 2018; Rönkkö et al., 2017; Rönkkö and Timonen, 2019). The pattern 353 of SA time-series is similar at both stations, but SA concentrations are lower at the street canyon. The highest sub-3 nm 354 particles and SA concentrations during both cases were measured at each site during the NPF event. The relation between

- sub-3 nm particles measured at the street canyon and background station during these case studies is presented in Fig.
- 356 S11. During the NPF event (Fig. 8a,b), sub-3 nm particles concentration at the background station is almost a factor of
- two higher than at the street canyon site. However, nearly simultaneous to the highest peak in sub-3 nm particles and SA
- 358 concentrations, a peak in particle concentrations across the modes (Fig 7b) as well as in SO<sub>2</sub> concentration (Fig. S7) is
- 359 observed at the background station. This suggests that the observation is related to a pollution plume (for example a ship
- 360 or a coal-fired power plant in Helsinki), which happens to be more efficiently transported to the background station than
- 361 to the street canyon. This illustrates the interplay of various types of sources on the aerosol concentrations, regional NPF
- 362 events, local traffic sources, and nearby point sources. It should be kept in mind that this case occurs during the weekend
- 363 when the traffic volumes are lower and daily patterns of traffic rate differ from weekdays, and thus on average the
- 364 influence of traffic on particle concentrations is expected to be more pronounced.



Figure 7. Time series of particle size distribution at the background station (b, d) and at street canyon site (a, c)
measured by DMPS for periods of 5 May 2018-7 May 2018 LT (a, b) and 8 May 2018 09:00-9 May 2018 15:00 LT
(c, d).



Figure 8. Time series of sub-3 nm particles (black) and SA (red) concentrations at the street canyon (a, c) and at the
background station (b, d) during 5 May 2018-7 May 2018 LT (a, b) and 8 May 2018 09:00-9 May 2018 15:00 LT (c, d).
Vertical blue lines indicate midnights. This figure with the logarithmic y-axis can be found in Supplementary material
(Fig. S12).

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#### 3.5. Regression analysis

376 To investigate in detail the contribution of different sources to the particle population at both sites, we analyzed 377 correlations of different variables with the concentrations of sub-3 nm particles, particles with a diameter between 3 and 7 nm  $(N_{3-7})$ , particles with a diameter between 7 and 25 nm  $(N_{7-25})$ , and Aitken mode particles  $(N_{25-100})$  (Table 3). Sub-3 378 379 nm particle concentration at the background station correlates best with the concentrations of  $SO_2$  (R = 0.64 on workdays 380 and R = 0.46 on weekends) and its oxidation product SA (R = 0.66 on workdays and R = 0.66 on weekends), which is a 381 common precursor of NPF. SO<sub>2</sub> and SA also correlate well with  $N_{3-7}$  at the background station, having slightly lower 382 correlation coefficients compared to sub-3 nm particles. There is no correlation between these variables and  $N_{7-25}$  or  $N_{25}$ . 383  $_{100}$  at the background station. A strong negative correlation (R= -0.57) between sub-3 nm particle concentrations and 384 cosines of wind direction at the background station during weekends indicates that during this time, high concentrations 385 of sub-3 nm particles are coming more likely from south than from north. Sub-3 nm particle concentration at the street 386 canyon correlates best with NO (R = 0.65 on workdays and R = 0.57 on weekends) and NO<sub>x</sub> concentrations (R = 0.62 on 387 workdays and R = 0.54 on weekends). Generally, at the street canyon site, high correlations are observed between particles 388 and species that can be associated with emissions from traffic: BC, NO<sub>x</sub>, NO, CO<sub>2</sub>. During workdays at the street canyon 389 site, the highest correlations for these variables are found for particles with a size between 3 and 7 nm, which corresponds 390 to the nucleation mode peak characteristic of primary emitted particles from traffic (Rönkkö & Timonen, 2019). The 391 correlation between sub-3 nm particles and SA at the street canyon site is also positive and relatively strong but during 392 workdays weaker than at the background station, which is in agreement with results from the case studies. Aitken mode 393 particle concentrations correlate well with BC during weekends at both stations, indicating that these particles have a 394 different combustion or biomass burning related origin from traffic. High correlations between  $N_{25-100}$  and CS can be 395 attributed to the fact that Aitken mode particles, especially those with diameters close to 100 nm, have a significant contribution to total aerosol surface area concentration and thus to CS. Overall, the correlation analysis suggests that the 396 397 particle population at the street canyon site is more influenced by traffic than at the background station. This is discussed 398 more for sub-3 nm particles in the next section.

## Table 3. Correlation between logarithmic values of N<sub>1-3</sub>, N<sub>3-7</sub>, N<sub>7-25</sub>, and N<sub>25-100</sub> and logarithmic values of other variables

- 400 during weekends and workdays at the street canyon and the background station. Correlations with a Pearson's correlation
- 401 coefficient higher than 0.5 are marked in bold. The sample size for this analysis is presented in table S1.

Darameter		Street canyon site				Background station			
rarameter		N <sub>1-3</sub>	N <sub>3-7</sub>	N <sub>7-25</sub>	N <sub>25-100</sub>	N <sub>1-3</sub>	N <sub>3-7</sub>	N <sub>7-25</sub>	N <sub>25-100</sub>
$SA [\#/cm^3]$	Workdays	0.49	0.40	0.27	0.27	0.66	0.55	0.16	0.02*
SA [#/em]	Weekends	0.61	0.50	0.33	0.21	0.66	0.51	0.31	0.01*
BC $[ng/m^3]$	Workdays	0.60	0.68	0.58	0.58	0.15	0.34	0.28	0.34
DC [lig/lil]	Weekends	0.33	0.37	0.29	0.50	0.27	0.29	0.20	0.53
$CS[s^{-1}]$	Workdays	0.29	0.51	0.51	0.67	-0.10	0.21	0.17	0.49
65[3]	Weekends	0.24	0.27	0.24	0.80	0.13	0.21	0.05	0.68
NO [nnh]	Workdays	0.65	0.73	0.60	0.56	0.37	0.39	0.34	0.30
	Weekends	0.57	0.50	0.40	0.36	0.45	0.40	0.19	0.16
NO [mah]	Workdays	0.62	0.71	0.60	0.56	0.28	0.39	0.22	0.31
TIOX [bb0]	Weekends	0.54	0.48	0.40	0.39	0.35	0.38	0.09	0.44

$O_2$ [nph]	Workdays	-0.09	-0.38	-0.38	-0.47	0.13	-0.04	-0.15	-0.34
03 [bb0]	Weekends	-0.24	-0.30	-0.31	-0.38	0.13	-0.09	-0.11	-0.24
CO <sub>2</sub> [nnm]	Workdays	0.38	0.47	0.44	0.53	-0.25	-0.05	0.06	0.28
CO <sub>2</sub> [ppin]	Weekends	0.56	0.43	0.40	0.44	-0.28	-0.04	0.00	0.32
SO <sub>2</sub> ** [nnh]	Workdays	-	0.28	0.16	0.31	0.64	0.59	0.24	0.34
50 <sub>2</sub> [ppo]	Weekends	-	0.28	0.07*	0.23	0.46	0.50	0.08	0.21
DII*** [0/ ]	Workdays	-0.43	-0.17	-0.12	-0.14	-0.15	-0.22	-0.25	-0.22
KII [/0]	Weekends	-0.47	-0.25	-0.24	-0.27	-0.11	-0.16	-0.14	-0.17
T*** [°C]	Workdays	0.38	0.21	0.15	0.13	0.17	0.33	0.18	0.05
1 [0]	Weekends	0.45	0.31	0.26	0.27	0.10	0.04	-0.09	-0.11
	Workdays	0.11/	0.24/	0.19/	0.12/	-0.36/	-0.19/	0.26/	0.05/
cos(WD)***/	WOIRdays	0.20	-0.01	-0.10	-0.03*	0.30	0.29	0.13	0.33
sin(WD)***	Waakanda	0.34/	0.34/	0.27/	0.01*/	-0.57/	-0.31/	0.04*/	-0.06*/
	WULKEIIUS	-0.01	-0.11	-0.18	-0.03*	0.20	0.25	0.16	0.45

402 403 \* Correlation not statistically significant at a significance level of  $\alpha = 0.05$ .

\*\* There is no overlap in measurements of SO<sub>2</sub> and sub-3 nm particle at the street canyon site.

404 \*\*\* Correlation calculated for logarithmic values of sub-3 nm particle concentration and standard values of the
 405 parameter.

406

## 3.6. Estimation of NPF and traffic contribution to sub-3 nm particles

407 We used the compounds that correlate best with sub-3 nm particles at each site, SA and NO<sub>x</sub>, as tracers for NPF and 408 traffic emissions, respectively. Using SA concentration as a tracer for NPF is based on the assumption that traffic is not 409 a major source of SA. We justify and discuss this assumption at the end of this section. To quantify the influence of each 410 process on sub-3 nm particle concentrations, we studied the dependency between sub-3 nm particles, SA, and  $NO_x$ 411 concentrations at both sites (Fig. 9, Table S2). We made bivariate fittings to common logarithms of  $NO_x$  and sub-3 nm 412 particles when the SA concentration was low and reversely we analyzed common logarithms of SA and sub-3 nm particles 413 when the  $NO_x$  concentration was low. The bins were chosen for fitting so that the bin limits at both stations, and the 414 sample size in each bin are comparable, and the bin width is either 0.25 or 0.5. The parameters characterizing the chosen 415 bins are presented in Table S2. The slopes of the bivariate fit to sub-3 nm particles and SA data for low NO<sub>x</sub> concentration 416 is close to 1 at both stations (Fig. 9 a,b). At the same time, the slope of the fit to sub-3 nm particles and  $NO_x$  data for low 417 SA concentration is considerably smaller at the background station (0.64) than at the street canyon site (1.40) (Fig. 9 c,d). 418 We investigated possible reasons for this difference such as constant background (local source) of sub-3 nm particles at 419 the background station or losses of sub-3 nm particles due to CS, or particle growth. Analysis of the correlation between 420  $NO_x$ , SA, and total particle concentration (Fig. S13), as well as the correlations between sub-3 nm particles,  $NO_x$ , SA, 421 and CS (Fig. S14-S15), implied that neither particle growth out of the sub-3 nm size range nor varying CS can explain 422 the difference in the slopes between stations. One possible explanation could be a constant production of sub-3 nm 423 particles at the background site, as a result of clustering of low-volatile organic vapors (Rose et al., 2018). Comparing ion 424 concentrations and sub-3 nm particles at the background station indicates that the constant source of ions in the 425 atmosphere cannot explain these high sub-3 nm particle concentrations at the background station (Fig. S16). One should 426 keep in mind that compared ranges of  $NO_x$  concentrations are different at each station. Additionally, particle evaporation 427 may affect the comparison.

428 Based on these bivariate fits, we estimated sub-3 nm particle concentration originating from NPF and traffic at the two 429 sites (Table 4). The analysis was done for the time when NO<sub>x</sub>, SA, and sub-3 nm particle concentrations were measured 430 at each station (Table A1, Fig. S17). The variability of estimated sub-3 nm particle concentration is high, and occasionally 431 estimated concentrations exceed the measured values of sub-3 nm particle while at other times estimated values are clearly 432 lower than the measured values (Fig. 10). However, our estimation captures the temporal variation of the sub-3 nm particle 433 concentrations adequately. We estimate that during the daytime (6:00-20:00), a similar fraction of sub-3 nm particles 434 originated from traffic (53%) and NPF (47%) at the street canyon site. At the background station, the daytime sub-3 nm 435 particle population was dominated by particles originated from NPF (74%). During the nighttime (20:00-6:00), the 436 influence of both sources on the sub-3 nm particles population was almost equal at the background station. At the street 437 canyon site, sub-3 nm particles originated mainly from traffic (65%) during the night. Overall, our results are consistent 438 with the fact that the regional NPF process occurs over a large spatial area, while traffic emissions are local.

439 When discussing the estimated relative contribution of traffic and NPF to the sub-3 nm population, we should keep in 440 mind that the conducted analysis does not consider the origin of SA. Traffic can directly or indirectly emit SA, thus traffic 441 may influence SA concentration used for estimating sub-3 nm particles formed during NPF. This could cause an 442 underestimation of the relative contribution of traffic to the sub-3 nm population. In order to estimate the significance of 443 this underestimation, we investigated the relations between SA and  $NO_x$  concentrations and between  $NO_x$  and  $N_{1-3}$ . We 444 found that even in the street canyon site, the variance in  $NO_x$  concentration explained at maximum only 7 % of the daytime 445 variance in SA concentration (Figure S18 and Table S3), which justifies the use of SA as NPF tracer. However, Olin et 446 al. (2020) estimated that during typical workday noon in May 2017, one year prior to the observations described here, 447 68% of SA concentration at the same street canyon site originated from traffic, which is not in line with our observations 448 for May 2018. The reason for this discrepancy is not known. Additionally, Olin et al. (2020) estimated that during May 449 2017, at typical workday noontime at the same street canyon site, the contribution of traffic to sub-3 nm particles was 450 approximately 85%, which is clearly higher than our estimate. The difference between our results and the ones presented by Olin et al. (2020) could be partly caused by the difference between the influence of traffic on SA concentration between 451 452 the two measurement campaigns, described above. Additionally, one needs to keep in mind that Olin et al. (2020) 453 calculated the traffic contribution to the sub-3 nm particles for a typical workday, while most of our data (57.8%) from 454 the street canyon site was collected at the time free from work. Overall, the differences between our results and those by 455 Olin et al. (2020) can indicate that even at the same site and at the same time of the year, the emissions and formation of 456 sub-3 nm particles may follow different mechanisms.

457 Generally, one should note that the estimates presented here are based on only a limited data set, and therefore it is not 458 expected to provide a complete picture of the contributions of NPF and traffic to sub-3 nm particles in Helsinki. The 459 relations between emissions of particles and NO<sub>x</sub> from traffic and between NPF and SA are expected to vary seasonally 460 or as a function of temperature (Gidhagen et al., 2005; Nieminen et al., 2014) and, consequently, the parameters derived 461 in this study are not expected to be valid through the year in Helsinki, even less in other locations. For instance, NPF 462 events are frequently observed in Finland in spring and autumn but very seldom in winter (Hussein et al., 2008), and 463 particle emissions from traffic are expected to be higher during colder temperatures in winter (Gidhagen et al., 2005). In 464 winter, the role of NPF events as a sub-3 nm particles source would probably be much smaller than what we estimated in 465 this study conducted in spring.



Figure 9. Correlation between the logarithm of SA and the logarithm of sub-3 nm particles colored by the logarithm of NO<sub>x</sub> (a) at the street canyon and (b) at the background station, as well as the correlation between the logarithm of NO<sub>x</sub> and the logarithm of sub-3 nm particles colored by the logarithm of SA (c) at the street canyon and (d) at the background station. Blue lines represent bivariate fit done to data with the logarithm of NO<sub>x</sub> smaller than 4 at street canyon site (a) or 3 at background station (b), or data with the logarithm of SA smaller than 5.5 at both stations (c,d). The parameters of the fit are presented as an equation on the plot. Subplots 9c and 9d have different limits of a x-scale.



472 Figure 10. The time series of sub-3 nm particles concentration measured during 4 May 2018-7 May 2018 LT (black) and
473 estimated based on NOx concentration (orange) and NO<sub>x</sub> and SA concentrations (red) (a) at the background station and
474 (b) at the street canyon site.

Table 4. The percentiles of the relative contributions of traffic and NPF to estimated sub-3 nm particle concentrations at the background station and the street canyon.  $[N_{1-3}]_{NOx}$  and  $[N_{1-3}]_{SA}$  present relative contribution of sub-3 nm particle concentrations estimated based on NO<sub>x</sub> and SA concentrations, representing the contributions of traffic and NPF, respectively. Equations used for calculating the relative contribution of each source are presented in Appendix (Eq. A5-A6)

	[N <sub>1-3</sub> ] <sub>NO2</sub>	x		[N <sub>1-3</sub> ] <sub>SA</sub>		
Percentile	25	50	75	25	50	75
Daytime						
Background [%]	9	26	30	70	74	91
Street canyon [%]	26	47	70	30	53	74
Nighttime						
Background [%]	41	67	75	25	33	59
Street canyon [%]	38	65	86	14	35	62
All campaign						
Background [%]	14	43	57	43	57	86
Street canyon [%]	32	54	78	22	46	68

## 480 4. Conclusions

In this study, for the first time, the particle size distribution in a diameter range from 1 to 800 nm was analyzed at two close-by stations in Helsinki. We found that the influence of traffic on particle number concentrations at the street canyon is most visible for sub-3 nm, nucleation mode, and Aitken mode particles, while at the background station the influence

484 of traffic is clear only for sub-3 nm and nucleation mode particles. By analyzing correlations between particle 485 concentrations and different trace gases, we conclude that sub-3 nm and nucleation mode particles are influenced by local 486 sources, especially traffic, while accumulation mode particles are dominated by long-range transportation from non-local 487 sources. Whether Aitken mode particles are more influenced by local or non-local sources, depends on the location. At 488 the background station, Aitken mode is largely dominated by non-local sources, while at the street canyon site this mode 489 is influenced by traffic.

We observed a very similar pattern in diurnal variation of SA concentration at both stations. Daytime SA concentrations
were slightly higher at the background station, likely due to a lower condensation sink than at the street canyon site.
During the nighttime, SA median concentration was similar at both stations.

Furthermore, we analyzed the relation of sub-3 nm particles with trace gases and meteorological variables during the whole measurement campaign. We observed that sub-3 nm particles at the background station are mainly related to  $SO_2$ and SA, while the sub-3 nm particle population at the street canyon was primarily associated with compounds linked to traffic emissions (BC,  $NO_x$ , NO, and  $CO_2$ ) and to a lesser extent with SA. Roughly similar dependencies wer obtained for the smallest nucleation mode particles in diameter range 3-7 nm, but for 7-25 nm and Aitken mode particles the association with  $SO_2$  and SA was clearly less pronounced at both sites.

499 Based on our observations, we developed a new method to estimate the relative contributions of traffic and NPF to sub-500 3 nm particle concentration at nearby urban sites. We uses NOx as a tracer for sub-3 nm particles originating from traffic 501 and SA as a tracer for NPF particles. Our results suggest that NPF had a stronger influence on the sub-3 nm particle 502 population than traffic at the urban background site, especially during the daytime. At the street canyon site, NPF and 503 traffic contributed to sub-3 nm concentrations rather equally. This indicates that traffic is an important source of sub-3 504 nm particles, but it does not solely dominate the sub-3 nm particle population at either of the studied sites in Helsinki 505 during the daytime in spring. However, in our estimation, we did not account for the origin of NPF precursors. SA and 506 other low-volatile compounds can be emitted by traffic and then participate in the formation of sub-3 nm particles. For 507 our data set, we showed that the SA emissions from traffic are clearly lower to photochemical SA formation, justifying 508 our estimates of distinguishing traffic and NPF particles based on SA and NOx concentrations. This might not be as 509 simple in other cases, since Olin et al. (2020) showed that at the same site in the previous spring, the traffic emissions 510 played much more significant role in SA concentrations.

Future studies should focus on different low-volatile compounds in an urban environment and investigate their influence on NPF. Additionally, analyzing the relative influence of different processes on the sub-3 nm particle population based on long-term measurements would be beneficial. In the future, the approach to estimate the contribution of NPF and traffic to particle number concentrations based on trace-gas concentration may be applied in other urban environments, which can improve the understanding of the effects of traffic on urban air quality. However, the variables, parameters and functions describing the traffic and NPF contributions may vary between sites and season, which leaves the determination of more universal functions to be the scope of future studies, with longer time series from different urban areas.

518 Appendix

519 Table A1. Working time of instruments used during the campaign.

Instrument	Model	Working period	Working			
			time [h]			
	Street canyon					
Particle Size Magnifier	Airmodus A11 nCNC	27.04.2018 13:00 - 02.05.2018 08:00	246			
(PSM ) fixed mode		04.05.2018 09:00 - 07.05.2018 15:00				
		08.05.2018 10:00 - 09.05.2018 14:00				
		10.05.2018 10:00 - 10.05.2018 14:00				
		11.05.2018 01:00 - 11.05.2018 17:00				
PSM step mode	Airmodus A11 nCNC	27.04.2018 00:00 - 15.05.2018 12:00	833			
		$15.05.2018\ 21:00 - 01.05.2018\ 00:00$				
Ultrafine	TSI 3776	27.04.2018 14:00 - 30.04.2018 07:00	548			
Condensation Particle		03.05.2018 19:00 - 06.05.2018 09:00				
Counter (UCPC)		08.05.2018 11:00 - 18.05.2018 16:00				
		21.05.2018 18:00 - 21.05.2018 22:00				
		24.05.2018 10:00 - 24.05.2018 12:00				
		24.05.2018 16:00 - 31.05.2018 10:00				
Condensation Particle	Airmodus A20	27.04.2018 14:00 - 17.05.2018 15:00	750			
Counter A20 (CPC)		17.05.2018 23:00 - 22.05.2018 10:00				
		24.05.2018 10:00 - 25.05.2018 14:00				
		26.05.2018 00:00 - 31.05.2018 10:00				
Differential Mobility	Vienna-type DMA coupled	27.04.2018 00:00 - 31.05.2018 23:00	840			
Particle Sizer (DMPS)	with Airmodus A20 DMA					
Atmospheric Pressure	TOFWERK AG	02.05.2018 00:00 - 03.05.2018 13:00	501			
Interface Time-Of-		04.05.2018 15:00 - 08.05.2018 09:00				
Flight Mass		08.05.2018 13:00 - 08.05.2018 15:00				
Spectrometer with the		08.05.2018 18:00 - 10.05.2018 09:00				
Chemical Ionization		10.05.2018 12:00 - 16.05.2018 09:00				
(CI-APi-TOF)		16.05.2018 12:00 - 22.05.2018 10:00				
		22.05.2018 12:00 - 24.05.2018 07:00				
SO <sub>2</sub> analyzer	43i-TLE	09.05.2018 12:00 - 10.05.2018 17:00	452			
		11.05.2018 09:00 - 11.05.2018 18:00				
		14.05.2018 09:00 - 31.05.2018 12:00				
CO <sub>2</sub> analyzer	LI-COR LI-7000	27.04.2018 09:00 - 24.05.2018 13:00	771			
		24.05.2018 16:00 - 29.05.2018 19:00				
	Bac	kground				
PSM fixed mode	Airmodus A11 nCNC	01.05.2018 10:00 - 10.05.2018 04:00	766			
		11.05.2018 08:00 - 05.06.2018 10:00				
PSM scanning mode	Airmodus A11 nCNC	04.05.2018 00:00 - 21.05.2018 11:00	671			
		21.05.2018 22:00 - 30.05.2018 05:00				
		02.06.2018 22:00 - 05.06.2018 00:00				

UCPC	TSI 3776	03.05.2018 17:00 - 10.05.2018 04:00	670
		11.05.2018 08:00 - 21.05.2018 16:00	
		25.05.2018 10:00 - 05.06.2018 10:00	
СРС	Airmodus A20	03.05.2018 11:00 - 10.05.2018 04:00	728
		$11.05.2018\ 08:00-20.05.2018\ 00:00$	
		21.05.2018 14:00 - 05.06.2018 10:00	
Twin Differential		01.05.2018 01:00 - 07.05.2018 14:00	821
Mobility Particle Sizer		$08.05.2018\ 09:00 - 05.06.2018\ 00:00$	
(Twin-DMPS)			
Neutral and Air Ion	Airel Ltd	26.04.2018 13:00 - 17.05.2018 02:00	932
Spectrometer (NAIS)		18.05.2018 21:00 - 06.06.2018 02:00	
CI-APi-TOF	TOFWERK AG	02.05.2018 15:00 - 04.06.2018 00:00	776
SO <sub>2</sub> analyzer		27.04.2018 01:00 - 07.05.2018 12:00	937
		08.05.2018 11:00 - 06.06.2018 00:00	
CO <sub>2</sub> analyzer		03.05.2018 18:00 - 14.05.2018 01:00	248

520 Table A2. Overview of additional variables used in this study measured at the background station and the street canyon

521 site.

Variable [unit]	Instrument / model	Height (m)			
Background station					
NO, NO <sub>x</sub> [ppb]	chemiluminescence analyzer / Horiba APNA 370	4			
O <sub>3</sub>	UV-absoption / Teledyne Instruments API 400E	4			
SO <sub>2</sub> [ppb]	UV fluorescence analyzer / Thermo Fisher Scientific TEI	4			
	43iTLE				
Relative humidity [%]	Vaisala HMP243	29			
Air temperature [°C]	Pentronic Pt100	4			
Wind direction [°]	2D ultrasonic anemometer/ Thies Clima 2.1x	32			
Wind speed [m/s]	2D ultrasonic anemometer/ Thies Clima 2.1x	32			
Global radiation [W/m <sup>2</sup> ]	Kipp and Zonen CNR1	32			
Black carbon	Multi Angle Absorption Photometer (MAAP), Thermo	4			
	Scientific, Model 5012				
Ion size distribution [cm <sup>-3</sup> ]	neutral cluster and air ion spectrometer (NAIS)	1.5			
	Street canyon				
NO, NO <sub>x</sub> [ $\mu g/m3$ ]	chemiluminescence analyzer / Horiba APNA 370	4			
O <sub>3</sub> [µg/m3]	UV fluorescence analyzer / Horiba APOA-370	4			
Relative humidity [%]	Vaisala WXT 536	4			
Air temperature [°C]	Vaisala WXT 536	4			
Wind direction [°]	Vaisala WXT 536	4			
Wind speed [m/s]	Vaisala WXT 536	4			

Black carbon	Optical analyzer / MAAP 5012	4
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## 522 Calculating the relative contribution of traffic and NPF to sub-3 nm particle population

Based on bivariate fittings on the common logarithms of sub-3 nm particles and SA when NO<sub>x</sub> concentration was low at the street canyon site (Fig. 9a), we determined Eq. A1 estimating the concentration of sub-3 nm particles formed during NPF ( $[N_{1-3}]_{SA}$ ) at the street canyon site. The same analysis conducted for the concentrations at the background station (Fig. 9b) resulted in Eq. A2. Correlation between common logarithms of sub-3 nm particles and NO<sub>x</sub>, when SA concentration was low, at the street canyon and background station (Fig. 9c-d) was used to determine Eq. A3 and A4, respectively. Equations A3 and A4 estimate the concentration of sub-3 nm particles emitted from traffic ( $[N_{1-3}]_{NO_x}$ ).

$$[N_{1-3}]_{SA} = 10^{-4.04} \cdot [SA]^{1.25}$$
(street canyon) (A1)

where  $[N_{1-3}]_{SA}$  is an estimated concentration of sub-3 nm particles formed during NPF, and [SA] is a SA concentration.

$$[N_{1-3}]_{SA} = 10^{-2.86} \cdot [SA]^{0.99}$$
 (background) (A2)

$$[N_{1-3}]_{NO_x} = 10^{-2.45} \cdot [NO_x]^{1.40}$$
 (street canyon) (A3)

where  $[N_{1-3}]_{NO_x}$  an estimated concentration of sub-3 nm particles emitted from traffic, and  $[NO_x]$  is a NO<sub>x</sub> concentration.

$$[N_{1-3}]_{NO_x} = 10^{0.59} \cdot [NO_x]^{0.64}$$
 (background) (A4)

Based on Eq. A1-A4, the relative contribution of traffic and NPF at each site was computed. To calculate the relative contribution of traffic ( $x_{[N_{1-3}]NO_x}$ ), the estimated concentration of sub-3 nm particles emitted by traffic was divided by the sum of estimated concentrations of sub-3 nm particles emitted by traffic and formed during NPF (Eq. A5). Similarly, the relative contribution of NPF ( $x_{[N_{1-3}]SA}$ ) was computed by dividing the estimated concentration of sub-3 nm particles formed during NPF by the sum of estimated concentrations of sub-3 nm particles emitted by traffic and formed during NPF (Eq. A6). The relative contribution of each source was calculated for the street canyon and the background station.

$$x_{[N_{1-3}]_{NO_x}} = \frac{[N_{1-3}]_{NO_x}}{[N_{1-3}]_{SA} + [N_{1-3}]_{NO_x}} \cdot 100\%$$
(A5)

where  $x_{[N_{1-3}]NO_x}$  is a relative contribution of traffic,  $[N_{1-3}]_{NO_x}$  is an estimated concentration of sub-3 nm particles emitted by traffic, and  $[N_{1-3}]_{SA}$  is an estimated concentration of sub-3 nm particles formed during NPF.

$$x_{[N_{1-3}]SA} = \frac{[N_{1-3}]_{SA}}{[N_{1-3}]_{SA} + [N_{1-3}]_{NO_x}} \cdot 100\%$$
(A6)

where  $x_{[N_{1-3}]SA}$  is a relative contribution of NPF,  $[N_{1-3}]_{NO_x}$  is an estimated concentration of sub-3 nm particles emitted by traffic, and  $[N_{1-3}]_{SA}$  is an estimated concentration of sub-3 nm particles formed during NPF.

#### 535 Data availability

Data used for this study is available at https://zenodo.org/record/4884875#.YLU8XedRUuU. DMPS, BC, O<sub>3</sub>,
meteorological data measured at the background station are available at the SmartSMEAR data repository
(https://avaa.tdata.fi/web/smart).

## 539 Author contribution

- 540 The main ideas were formulated by TP, PP, JKo, HK, JVN and the results were interpreted by MOk, JKo, HK, PP, and
- 541 TR. HK, MA, KT, HL, LS prepared measurement methodology and OG, HK, MOI, RB, HP, MA, HL, and LS contributed
- to data collection. MOk, HK, KT, RB performed the data analysis. Instruments were calibrated by MOl, JKa, YJT, and
- 543 RB. MS, TP, TR, HT, JVN coordinated project while JKo, OG, PP, JKa, and HT supervised it. MS, TP, HT, TR made a
- 544 funding acquisition. MOk visualized data and prepared the manuscript with contributions from other authors. All the
- authors reviewed the manuscript.

## 546 Competing interests

547 The authors declare that they have no conflict of interest.

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